PATENT APPLICATION

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METHOD FOR DYEING COTTON WITH INDIGO

BACKGROUND OF THE INVENTION

[0001] Field of the Invention

[0002] This invention relates to the dyeing of cotton and blended fabric materials, in the form of yarn, fabric, or articles of clothing, in a batch or continuous process.

[0003] Summary of the Background Art

[0004] Indigo, being one of the longest-known coloring agents, has been used to dye cellulose-based textiles, such as cotton, for centuries. However, since indigo is practically insoluble in water, ether, alcohol, and dilute acids, conventional dyeing processes include reducing the indigo dye to a soluble leuco form having an amber color, using a suitable reducing agent with an alkaline material. After the fabric material is then exposed to the leuco form in a bath, the fabric material is exposed to air or oxygen so that the reduced dye within the fabric is oxidized, returning to an insoluble form in which the blue color is apparent. Since, even in the leuco form, indigo has a low affinity for cellulosic materials, these steps are repeated as often as needed to obtain the desired shade of blue, with five to seven immersions typically being used, and with each of these immersions being followed by an oxidation process.

[0005] Commercially successful processes for dyeing cotton fabrics with indigo have been generally limited to continuous processes for dyeing warp yarn to be

used in the production of blue jeans and other denim products. Such a continuous process is described, for example, in U.S. Pat. No. 3,457,022 as a process in which the yarn is first dipped in hot dye solutions to achieve maximum penetration of the dye within the yarn, which is then repeatedly dipped in cold dye solutions to obtain the desired color.

[0006] Other patents describe the chemical components of the dye bath. For example, U.S. Pat. No. 4,166,717 describes a process in which the indigo is reduced to its soluble leuco form with sodium hydrosulfate and maintained in an aqueous solution with sodium hydroxide. An aldehyde addition product, such as formaldehyde, acetaldehyde, or furfural, is added to the solution, with an adduct, such as a bisulfate or a sulfoxylate.

[0007] U.S. Pat. No. 5,935,273 describes a process for the continuous dyeing of yarn containing cellulose in a single passage through an aqueous solution of indigo in its reduced, or leuco, state in a dye liquor additionally containing deoxidants, alkali, and a dissolved alkali metal salt at a concentration of 100 to 200 grams/liter as an electrolyte as a pH value of the liquor is adjusted to about 10.2 to 11.3. As the electrolyte concentration is maintained, the yarn is exposed to a gas that dissolves in the aqueous solution while forming an acid. Suitable gasses are carbon dioxide, hydrogen chloride, formic acid vapor, and acetic acid, with carbon dioxide being preferred, with the use of carbon dioxide to establish maintain and control pH in dyeing processes being further discussed in U.S. Pat. No. 5,295,998, and with the use of carbon dioxide to effect an accelerated neutralization of cellulose textile substrates being additionally discussed in U.S. Pat. No. 4,536,907. Then the reduced indigo in the yarn is oxidized to form a pigment, with the dyeing process.

[0008] The conventional process includes labor-intensive steps associated with the handling of the yarn, such as warp beam make-up and yarn quilling. To eliminate such steps, what is needed is a method for dyeing garments instead of

the yarn used in their production. Additionally, dying garments provides for effective inventory control, and for the color coordination of garments containing different types of yarns or knitted and woven materials.

[0009] U.S. Pat. No. 4,845,789 describes a process for the rapid dyeing of a series of successive garments or batches of garments with a vat dye, preferably indigo dye. While the garments are being constrained, they are submerged in, and impregnated with, a dyeing solution in a first bath. Then, they are removed from the first bath and held with the draining from them to be conserved for reuse. Next, the garments are promptly immersed in an oxidizing solution in a second bath to shock oxidize the dye present in the garments, which are then removed from the oxidizing bath while draining the oxidizing solution and preserving it for reuse. The garments are then washed and dried. The time between removal of the garments from the dyeing solution and their placement in the oxidizing solution is less than five minutes.

[0010] U.S. Pat. No. 4,756,037 describes a process for dyeing with a vat dye, such as an indigo dye solution, a series of successive garments made with fabric containing cellulose. The garments are supported on supports that keep all fabric surface3s of each garment accessible to treating solutions, so that the materials are uniformly impregnated with a dye solution at a first bath. The garments are then inserted in an oxidizing solution within a second bath to uniformly oxidize the dye present within each garment.

[0011] The patent art additionally describes a number of methods for treating cellulosic material and blends including cellulose to improve dyeability for dye materials other than indigo. For example, a method for producing anionically dyeable smooth dry crosslinked cellulose is described in U.S. Pat. No. 5,298,584, with a cellulose-containing material being modified with a combination of a hydroxyalkylamine or a hydroxyalkyl quaternary ammonium salt, one or more glycols, and a crosslinking agent. The reaction is typically catalyzed with salts

such as zinc nitrate or magnesium chloride, used either alone or in conjunction with citric acid. Types of usable anionic dyes include acid, direct, and reactive dyes. The cellulose-containing material may be in the form of fibers, yarns, slivers, and paper. U.S. Pat. No. 5,139,530 describes the production of anionically dyeable smooth-dry crosslinked cellulosic materials by treatment of methylolamide crosslinked cellulosic materials with an alkali swelling agent such as sodium hydroxide before dyeing. U.S. Pat. No. 3,576,589 describes a method for dyeing a fabric, such as a polyester/cotton fiber, in a vat/disperse dye system, using hydroxylamine sulfate under conditions of thermal fixation. The hydroxylamine sulfate is maintained at a pH in the range 5.0 to 6.5 in a vat/disperse dye pad to obtain maximum penetration of the dye within the fibers of the fabric. U.S. Pat. No. 4,767,421 describes a method of manufacturing a homogeneous water-insoluble dye layer on a substrate, with a solution of a cationic or anionic dye in an organic solvent being provided on the substrate, with the solvent being removed, and with the resulting dye layer being treated with am aqueous solution of a salt. The cation of the anionic dye is exchanged for the cation of the salt. Alternately, during treatment with an aqueous solution of a salt or acid, the anion of the cationic dye is exchanged for the salt or acid.

[0012] What is needed is a method for dyeing fabrics and garments formed from fibers including cellulose with indigo, as well as for dyeing the yarn used to make such fabrics and garments. Additionally, what is needed is a method for dyeing fibers including cellulose without relying on multiple dips to get a suitable shade. Furthermore, what is needed is a method allowing the use of batch processes, such as pad-jig dyeing and dyeing within a rotary dyeing machine to dye cellulosic materials with indigo.

SUMMARY OF THE INVENTION

[0013] In accordance with an aspect of the invention, a method is provided for dyeing a cellulosic material. The method includes:

[0014] preparing a dyebath including particles of indigo pigment and a first substance causing the particles of indigo pigment to become electrically charged in a first polarity;

[0015] preparing the cellulosic material for dyeing by applying a second substance to the cellulosic material to form a substrate on the cellulosic material having an ionic charge with a polarity opposite the first polarity;

[0016] immersing the cellulosic material prepared for dyeing in the prepared dyebath to cause the particles of indigo pigment to be ionically attracted to the substrate and retained thereon;

[0017] chemically reducing the particles of indigo retained on the substrate to form a soluble leuco form entering the cellulosic material; and

[0018] oxidizing the soluble leuco form to form indigo pigment within the cellulosic material.

[0019] The cellulosic material to be dyed may be a cotton fiber or a blend of cotton and synthetic fibers, in the form of yarn, woven or knitted cloth, or garments.

[0020] Preferably, the first polarity is negative, with the first additive being an anionic acrylic copolymer, while the second additive is a cationic polyamide or polyamine.

[0021] The method may be performed in a rotary dyeing machine, with multiple baths being added and drained between the process steps, in a pad-jig process, with the cellulosic material being fed entirely through multiple baths

added and drained within a jig bath vessel, or in a continuous process, with the cellulosic material simultaneously moving through multiple baths.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] FIG. 1 is a flow chart showing the steps of a batch process performed according to the invention within a rotary dyeing machine;

[0023] FIG. 2 is a schematic view of apparatus performing a pad-jig version of the process of FIG. 1; and

[0024] FIG. 3 is a schematic view of apparatus performing a continuous version of the process of FIG. 1.

DETAILED DESCRIPTION OF THE INVENTION

[0025] In accordance with the present invention, a dyebath is prepared for dying cellulosic material, with an indigo dye in its pigment form being mixed with a first additive, causing the indigo particles to become electrically charged in a first polarity. For example, an anionic acrylic copolymer is used as the first additive in an aqueous bath to make the particles take on a negative charge, making the treated particles anionic. As the particles become charged in this way, they also become rapidly and evenly dispersed within the bath, apparently due to the fact that these similarly charged particles repel one another.

[0026] The cellulosic material to be dyed may be a cotton fiber or a blend of cotton and synthetic fibers, in the form of yarn, woven or knitted cloth, or finished articles of clothing. In accordance with the present invention, this material is prepared by treatment with a second additive causing a substrate to be formed on the cellulosic material, with the substrate having an ionic charge opposite in polarity to the charged pigment particles. For example, if the pigment particles are negatively charged, the cellulosic material is treated with a second additive, such as a cationic polyamide, causing a cationic substrate to be formed. Such a

material additionally crosslinks to form a strong bond with the cellulosic material. Preferably, this process is continued until the dyebath is exhausted, with essentially all of the indigo pigment being transferred to the cellulosic material.

[0027] Following immersion in the dyebath, the cellulosic material placed in a reduction bath with the ionic bonds continuing to hold the indigo pigment in place on the substrate. In the reduction bath, the indigo pigment is reduced to its soluble leuco form to enter the fibers of the cellulosic material.

[0028] Following the reduction bath, an oxidation process is applied to return the dye in its leuco state to its blue pigment form. Oxidation may be accomplished in several ways. For example, if the cellulosic material is a roll of fabric, the fabric may be opened and passed through a vacuum extractor to pull liquids from the fabric. Then, the fabric is fed around cold cylinders. Alternately, the cellulosic material may be passed through a chamber in which it is exposed to ozone for a few seconds. The ozone oxidizes the dye and removes most of the sulfites that otherwise interfere with indigo fixation. If the cellulosic material is a garment being dyed in a batch process within a rotary machine, ozidation occurs while the garments are tumbled without water, with the door of the machine open, or with air being pumped into the machine while the garments are drying. Following oxidation in air, the garments are preferably rinsed with peroxide and acetic acid to remove sulfites.

[0029] This process avoids a problem associated with the limited affinity of indigo in its soluble leuco form for cellulosics. This problem has limited the application of the leuco form to cotton materials in the conventional process to about 0.3% of the weight of the cotton materials per dip, with about 2% being needed to produce a deep shade upon subsequent oxidation to the pigment state. Therefore, the conventional process typically requires five to seven dips, with oxidation occurring between dips. On the other hand, it has been found such a limitation does not exist when indigo is applied in its pigment form to the

surface if a textile material. For example, the process of the invention can readily be used in an exhaust bath to apply pigment equaling 3% of the weight of the textile material. Thus, a single application of dye according to the present invention produces the same shade as a conventional process including four to seven separate immersions in indigo in its leuco form, each of which is followed by oxidation.

[0030] FIG. 1 is a flow chart showing the steps of a batch process performed according to the invention within a rotary dyeing machine. For example, this process is used to dye garments in accordance with the present invention, with the garments first being scoured and rinsed in step 10. Next, in step 12, the garments are prepared for dyeing, by being tumbled within the rotary machine in an aqueous bath, including the phosphated alcohol sold as Penetrant EH equal in weight to 0.5% of the weight of the garments, a cationic polyamide equal in weight to 7% of the weight of the garments, at a temperature of 43°C (110°F) for 15 minutes. Alternatively, a similar weight of cationic polyamine may be added to the bath. After this step is completed, the rotary machine is drained.

[0031] In step 14, an aqueous dyebath is prepared, being composed of indigo powder having a weight equal to 2% of the weight of the garments and an ionic acrylic copolymer, also having a weight equal to 2% of the weight of the garments. Alternately, liquid indigo paste having a weight equal to 20% of the weight of the garments can be used. The dyebath is prepared in hot water before being introduced into the rotary machine to start step 16.

[0032] In step 16, the garments are tumbled within the rotary machine in the dyebath prepared in step 14, with a phosphated alcohol sold as Penetrant EH equal in weight to 1% of the weight of the garments being dyed being added to the dyebath, along with magnesium sulfate equal in weight to 4% of the weight of the garments. After the garments have been tumbled in this dyebath for 12 minutes, calcium chloride equal in weight to 1% of the weight of the garments is

added, with the garments being tumbled for an additional 5 minutes. Then the bath, which should be clear at this time, is drained.

[0033] In step 18, an aqueous reduction bath is prepared at 32°C (90°F), with the phosphated alcohol sold as Penetrant EH equal in weight to 1% of the weight of the garments being added to Epsom salt equal in weight to 2% of the weight of the garments. Then, sodium hydroxide is added to bring the pH to 11-11.5, with a 50% solution of the sodium hydroxide being, for example, approximately equal in weight to about 16% of the weight of the garments. Next, sodium hydrosulfite is added at a level of 6-10 grams per liter of bath, having a weight, for example, of about 32% of the weight of the garments.

[0034] In step 20, the reduction bath prepared in step 18 is added to the rotary machine, with the garments being tumbled until they take on a yellow green shade, indicating that the indigo pigment has been reduced to its leuco form. Then, the reduction bath is drained, with the machine continuing to run. Then, in step 22, the machine is switched from tumble mode to a light extraction mode to extract some of the liquid. Then, in step 24, the door of the rotary machine is opened, or air is alternately pumped into the machine, while the garments are tumbled until they appear indigo blue, due to the oxidation of the dye material in its leuco form to its pigment form. This takes about seven minutes.

[0035] Next, in step 26, a new bath is drawn at 43°C (110°F) for washing the garments. First, a 50% solution of hydrogen peroxide, weighing 0.5% of the weight of the garments, and glacial acetic acid, weighing 0.6% of the weight of the garments, are added to the bath, in which the garments are tumbled for five minutes. Then, a detergent having a weight equal to 0.5% the weight of the garments is added, and the garments are tumbled for another five minutes. Then, the bath is drained, and the garments are rinsed briefly.

[0036] Then, in step 28, a finish bath is drawn at 43°C (110°F) to apply a finish

for wash and crock fastness of the dyed garments. A soft acrylic binder, having a weight equal to 2% of the weight of the garments, is added to the finish bath, along with polyamide having a weight equal to 2% of the weight of the garments. The garments are tumbled for in this bath for fifteen minutes. Then, the bath is drained, and the machine is run in an extract mode to extract the liquid. Finally, in step 30, the garments are tumbled dry, curing the finish applied in step 28.

[0037] FIG. 2 is a schematic view of apparatus performing a pad-jig dying process used, for example, to dye a roll 36 of woven cellulosic material in accordance with the present invention. For this process, the pad vessel 38 is filled with a bath 40 including the phosphated alcohol sold as Penetrant EH having a weight equal to 1% of the weight of the woven material to be dyed, together with a cationic polyamide having a weight equal to 7% of the weight of the material to be dyed. During the padding process, the woven material is squeezed, together with liquid taken up with the material, between rollers 42 before being wound onto a take-up roll 44. During this padding process, the material is entirely moved through the bath 40, since the pad vessel 38 is shorter than the material in the direction in which the material is moved.

[0038] After the padding process is completed, the material from the take-up roll 44 is moved to serve as a first roll 46 for a jig bath vessel 48. Material is then moved between the first roll 46 and a second roll 50 in either direction, with the material being pulled through a bath 52 in the vessel 48. Rolls 54 are used to squeeze fluids from the bath into the material before it is rolled onto the first roll 46, and rolls 56 are used to squeeze fluids from the bath into the material before it is rolled onto the second roll 50. During each process of the material occurring within the jib bath vessel 48, the material is entirely moved through the bath 52 within the jig pad vessel at least once, since the jig bath vessel 48 is shorter than the material in the direction in which the material is moved.

[0039] The jig bath vessel 48 is first filled with water for an overflowing rinse of

the material taken from the padding process. During a first rinse, the material is moved through the bath 52 twice, from one end to the other and back again. Next, the rinse water is drained, and the jig bath vessel 48 is filled with a dyebath having a temperature set at 38°C (100°F). The phosphated alcohol sold as Penetrant EH is added to the dyebath, in an amount having a weight equal to 1% of the weight of the material being dyed, along with magnesium sulfate having a weight equal to 4% of the weight of the material. Then, indigo pigment having a weight equal to 2% of the weight of the material to be dyed, having been previously treated with an anionic acrylic copolymer also having a weight equal to 2% of the weight of the material is then added to the dyebath. The material is then run through the dyebath within the jig pad vessel four times from one end to the other four times. Calcium chloride having a weight equal to 4% of the weight of the material being dyed is then added to the dyebath, with the dyeing process being continued while the material is run through the dyebath six additional times.

[0040] Then, the dyebath within the jig bath vessel 48 is drained, and a reduction bath that has been prepared at 32°C (90°F) is added to the vessel 48. The reduction bath is an aqueous bath composed of the phosphated alcohol sold as Penetrant EH in a weight equal to 0.5% of the weight of the material being dyed, of Epsom salt having a weight equal to 1% of the weight of this material, of sodium hydrosulfite having a weight equal to 16% of the weight of this material, and of a 50% solution of sodium hydroxide having a weight of 8% of the weight of this material. The material is then run through the reduction bath four times from one end of the material to the other.

[0041] Next, the reduction bath is drained from the jig bath vessel 48, and an oxidation bath that has been prepared for oxidation of the dye material is added to the jig bath vessel 48. This oxidation bath is an aqueous bath comprising sodium bromate at a concentration of 2 grams per liter of water and glacial acetic

acid at a concentration of 0.5 grams per liter of water. The material is run through the oxidation bath, held at 43°C (110°F) twice from one end to the other. Then, this oxidation bath is drained from the jig bath vessel 48, which is refilled with the oxidation bath, having the same temperature and concentration of chemicals, and the material is run through the oxidation bath two more times. This process is then repeated, so that the material is treated with three separate oxidation baths.

[0042] After the third oxidation bath has been drained from the jig bath vessel 48, a wash bath is prepared at 43°C (110°F) within the jig bath vessel 48. The wash bath is an aqueous bath initially composed of a 50% solution of hydrogen peroxide having a weight equal to 1% of the weight of the material being dyed. The material is run twice through this wash bath from one end of the material to the other. Then, a detergent having a weight equal to 0.3% of the weight of the material is added to the wash bath, and the temperature of the bath is raised to 49°C (120°F), before the material is run through the wash bath three more times from one end to the other. After the wash bath has been drained, water is added to the jig bath vessel 48 as the material is run through the vessel 48 twice from one end to the other for overflowing rinses.

[0043] After the rinse water is drained from the jig bath vessel 48, this vessel 48 is filled with a finish bath including an acrylic binder having a weight equal to 3% of the weight of the material being dyed and a polyamide having a weight also equal to 3% of the weight of the material being dyed. The material is then run through this finish bath from one end to the other of the material four times. In the last pass through the finish bath, the material is not rewound on roll 50, but is rather passed through a vacuum extractor 58 for removal of the liquid, and is dried by being pulled over a number of rolls 60, through which hot air is circulated to hold the rolls 60 at 138°C (280°F). Then, the finish of the material, which has been applied in the finish bath, is cured at 160°C (320°F) on a frame 62 within an

enclosure 64, before the material is wound on a take-up roll 66.

[0044] FIG. 3 is a schematic view of apparatus performing a continuous dyeing process used, to dye a roll 70 of woven cellulosic material in accordance with the present invention. In the continuous dyeing process, the steps of the invention are performed simultaneously in apparatus arranged so that the steps are performed in the described order on each section of the woven cellulosic material as it is run through the apparatus.

[0045] The woven material from the supply roll 70 is first run through a preparation bath 72 in a first vessel 74 to be prepared for dyeing by being coated with a cationic polyamide. The preparation bath 72 is preferably operated at 65°C (149 °F), with the concentration of the cationic polyamide being held at a level causing the material picks up 7% of its weight in cationic polyamide. Then, the material is dried on cylinders 76 held at 129°C (265°F) by hot air flowing through the cylinders.

[0046] After exiting the heated cylinders 76, the material is run through a dyebath 78 in a second vessel 80. The dyebath 78 is preferably an aqueous bath held at 43°C (110°F) includes powdered indigo pigment dispersed with an anionic acrylic copolymer having a concentration held to match the concentration of the indigo pigment. The concentration of the indigo pigment is preferably held at a level causing the material to take up 2% of its weight in pigment from the dyebath 78. Then, the material is dried on cylinders 82 held at 129°C (265°F) by hot air flowing through the cylinders.

[0047] After exiting the heated cylinders 82, the material is run through a reduction bath 84 in a third vessel 86. The reduction bath 84 preferably is an aqueous bath including 45 grams per liter of water of sodium hydrosulfite and a similar concentration of a 50% solution of sodium hydroxide to convert the indigo pigment to its water-soluble leuco form. The material is transported from the

reduction bath 84 to an airless steamer 88 operating at a temperature of 104°C (220°F), which is preferably configured so that an area of the material is steamed for one minute within the steamer 88. After exiting the steamer 88, the material is pulled through an oxidation chamber 90 fed by a corona discharge ozone generator 92 producing 100-300 grams per hour. Within the chamber 90, the dye in its leuco form is oxidized, being returned to its pigment state. The exposure of the material to ozone additionally promotes the removal of sulfites within the material. Alternately, the material may be oxidized by exposure to oxygen or by being run through a bath including sodium bromate and acetic acid.

[0048] After leaving the oxidation chamber 90, the material is fed into a wash bath 94, including water held at 60°C (140°F) and a non-ionic detergent, within a wash box 96. Then, the material is fed through a plain water rinse 98 held at 43°C (110°F) at a rinse vessel 100, before being dried on heated cylinders 102 held at 129°C (265°F). From the heated cylinders 102, the material is run through a finish bath 104 within a finish vessel 106 including an acrylic binder, such as the product sold as RHOPLEX K-3, and polyamide. After exiting the finish bath 104, the material is dried on heated cylinders 108, which are also held at 129°C (265°F). Then the material is cured at (325°F) on a frame 110 2ithin a chamber 112 for one minute. Finally, the finished material is rolled on a take-up roll 114.

EXAMPLE 1

Dyeing Knitted and Woven Cotton Garments in a Rotary Machine with a Combination of indigo Pigment and Another Organic Pigment

[0049] In a first exemplary application of the invention, knitted t-shirts made of cotton and woven cotton dress shirts were dyed in a rotary machine turning at 18 rpm with indigo and with another organic pigment. The process described above in detail in reference to FIG. 1 was used, except as noted below. This process

produced garments that were dyed a very bright full navy blue color.

[0050] In step 10, the garments were scoured for fifteen minutes at (180°F) with an industrial soap, sold under the name LT SPECIAL, followed by a rinse for 10 minutes at (120°F). In step 14, the dyebath was prepared with a combination of indigo powder having a weight equal to 1.5% of the weight of the garments, and a phthalocyanine organic pigment, also having a weight equal to 1.5% of the weight of the garments. The dyebath was pasted with the anionic acrylic copolymer having a weight equal to 3% of the weight of the garments before hot water was added to the mix. In step 20, both the garments and the reduction bath turned a green color formed by the combination of the yellow-green color of indigo in its leuco state, together with blue color remaining within the phthalocyanine pigment in just six minutes, when the reduction bath was drained. In step 24, the garments oxidized to a bright blue color in fifteen minutes. In the final portion of step 26, the garments were rinsed in cold water for five minutes.

EXAMPLE 2

Dyeing a Cotton Fabric in a Pad-Jig Process with Indigo Pigment

[0051] In a second exemplary application of the invention, 12-ounce cotton twill is dyed in the pad-jig process described above in reference to FIG. 2. Before beginning the process, the fabric is desized and scoured. During padding within the pad vessel 38, the fabric picks up about 71% of the polyamide in the bath 40. After the oxidation baths within the jig bath vessel 48, the roll of fabric iscompletely oxidized to a true indigo blue color, and the bath is clear.

EXAMPLE 3

Continuous Pad Steam Dyeing of a Cotton Corduroy Fabric with Indigo

[0052] In a third exemplary application of the invention, a corduroy cotton fabric material was desized, scoured, and bleached. Then, the material was dried and run through the process described in detail above in reference to FIG. 3.

[0053] While the invention has been described in its preferred forms or embodiments with some degree of particularity, it is understood that this description has been given only by way of example, and that many changes can be made without departing from the spirit and scope of the invention, as described in the appended claims.